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Preliminary Evaluation of a Method Using an FID (Flame Ionization Detector) for Measurement of Methanol in Auto Emissions

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PRELIMINARY EVALUATION OF A METHOD USING AN FID FOR MEASUREMENT OF METHANOL IN AUTO EMISSIONS

by

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ABSTRACT

This report evaluates a simplified technique for estimating methanol emission rates in auto exhaust. The technique, referred to as the FID Bubbled Method or FBM, is based in priciple on the fact that while hydrocarbons are not readily absorbed in water, methanol is. Hence, by using a heated flame ionization detector to measure the organic mass in samples before and after bubbling them in water, the quantity of methanol originally present can be estimated by taking the difference between the measurements. Evaluation of the method was done by comparing methanol measurements using the FBM with measurements made using an established reference method. Results showed poor to fair agreement between the two methods. The FID Bubbled Method appeared better at estimating methanol emission rates from evaporative tests than from exhaust tests and also exhibited better accuracy for samples containing higher levels of methanol.

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SECTION 1
INTRODUCTION

In August 1986, the EPA published a notice of proposed rulemaking for standards for emissions from methanol-fueled motor vehicle engines(1). Since that time, comments regarding the proposed standard have been solicited from a number of automobile manufacturers. Of the comments received, many have addressed the "overly complex" instrumentation requirement set forth in the standard for measurement of organic compounds. In accordance with the proposed standard, gas and liquid chromatographs (GCs and LCs) would be required for methanol and formaldehyde analyses in addition to the heated flame ionization detector (FID) required for regulated hydrocarbon analyses.

The consensus of recommendations received from commentators proposes that the separate measurements of methanol and formaldehyde not be required, thus eliminating the need for GC and LC analyses. Manufacturers contend that reasonably accurate measurement of total organics can be had through the sole application of a heated FID, in one form or another. Some further suggest or recommend the use of correction factors to account for differences in FID response and photochemical reactivity between the organic components.

With regard to these comments, the concerns of instrument complexity are valid and sole use of the heated FID to measure total organics would greatly simplify the procedure. The use of a correction factor to compensate for the FID's low response to methanol would be appropriate if the fraction of methanol to total organic emissions remained constant; however, the fraction varies significantly with fuel type and vehicle. For example, 80 percent of the FTP total organic emissions were methanol from a methanol-car tested in 1984 versus 60 percent for one tested in 1986 (2,3). Both vehicles were Methanol Escorts, but the earlier tests were performed using a 90 percent methanol fuel while the later tests used an 85 percent methanol fuel.

This study was undertaken to evaluate a simplified method for estimating methanol emissions from automobiles using a technique which employs a heated FID. Based in principle on the high solubility of methanol and low solubility of hydrocarbons in water, the technique measures total organics of the sample with the FID, bubbles the sample through water to remove the methanol portion, then remeasures the remaining organic fraction with the same FID. The difference between the total organics (initial FID measurement) and the remaining organics (final FID measurement) is corrected for FID response to methanol and taken as an estimate of the sample's methanol concentration.

While it is known that any hydrocarbons which would be absorbed in solution during the bubbling process would be counted as methanol by the method, the impact of this occurrence on the technique's accuracy requires investigation. Because a greater quantity of the more soluble automobile hydrocarbon emissions occur immediately following a cold start, the highest methanol measurement errors with the technique likely occur during the FTP cold transient test phase (Bag I). On the other hand, the lowest errors likely occur with evaporative emissions which contain relatively few water soluble hydrocarbon components.

SECTION 2
CONCLUSIONS AND RECOMMENDATIONS

An experimental study was carried out to evaluate a simplified method (FID Bubbled Method) for measuring methanol emissions from a methanol-fueled automobile. Conclusions based on a comparison of results obtained using the GC method (reference method) and the FID Bubbled Method (FBM) are as follow:

1. Comparisons between the FBM and GC method for methanol measurement are fair to poor with differences between methods ranging from 11 to 112 percent (see Table 1).
2. Comparison between the methods is better with methanol evaporative emissions than with methanol exhaust emissions.
3. Methanol measurement differences, expressed as a percent of the GC value, are inversely related to the methanol content of exhaust samples.
4. Accuracy of the FBM is compromised by the absorption of hydrocarbons in water, particularly during the CT (cold transient) Test Phase of the FTP.

Not all of the difference between GC and FBM methanol measurements could be attributed to the absorption of hydrocarbons in the water solution used for removal of the methanol. When FBM methanol measurements were corrected to account for the loss of the soluble hydrocarbons, the resulting values were still significantly higher than those from the GC. Another factor thought to perhaps have an impact on FBM accuracy by altering the FID's response to normal hydrocarbons was the increase in humidity of the bubbled sample compared to the unbubbled sample. Preliminary tests were carried out to qualify any effect this factor might be having on analyzer response but no significant effect was observed. Future tests are recommended to thoroughly examine the humidity effect on FID response to organic emissions samples from a methanol-fueled automobile.

SECTION 3
EXPERIMENTAL PROCEDURES

The procedure adopted was designed to enable an evaluation of a simplified technique for measuring methanol emissions from a methanol-fueled automobile. Basically it consisted of comparing methanol mesurements made using a technique known as the FID Bubbled Method or FBM with measurements made using an established reference method. The reference method utilized a gas chromatograph (GC) to analyze methanol which had been trapped in a chilled water solution (4).

TEST VEHICLES AND FUELS

The principal test vehicle used to generate methanol emissions for the study was a Methanol Escort which was equipped with a 3-way catalyst. It was a modified version of its gasoline-fueled counterpart designed to operate on "nearly neat" methanol fuel. Engine modifications featured an increased compression ratio, recalibrated carburetor, and a retimed ignition system. Many of the parts in the Escort's fuel tank and fuel delivery system had been replaced with materials designed to withstand the corrosive effects of methanol.

Experiments with the Methanol Escort were carried out in a "piggyback" fashion as testing proceeded during a higher priority program. When tests on the Escort were concluded, a few exhaust samples were obtained from a conventionally fueled, 1987 Plymouth Caravelle. These were combined with appropriate quantities of methanol to simulate a methanol car's exhaust, then used to examine the effects of methanol and sample humidity on FID response to hydrocarbons. Use of the Caravelle for these purposes was justified because the character of exhaust hydrocarbons from a methanol car was found to resemble that from similarly controlled gasoline-fueled cars (2).

Fuels used by the Methanol Escort during the study were M85 (85 percent methanol/15 percent unleaded winter grade gasoline) and M100 (pure methanol). The owner's manual for the Escort recommended use of M85 because the gasoline fraction of the fuel provides good front-end volatility for engine starting in cold weather. Runs with M100 were conducted to assist in evaluating the FBM over a wider range of possible methanol emission rates and exhaust gas compositions. Regular unleaded wintergrade gasoline was used in the experiments conducted on the Plymouth Carvelle.

SAMPLE GENERATION, COLLECTION, AND ANALYSIS

The Methanol Escort was driven through a series of FTP driving cycles on an electric chassis dynamometer. For each test run, three sets of exhaust data were obtained corresponding to the cold transient (CT), hot stabilized (HS), and warm transient (WT) test phases. Evaporative emissions were collected only during the diurnal tests.

Exhaust gases from the car were ducted into a dilution tunnel where they were thoroughly mixed with filtered diluent. The diluted exhaust gas mixture was drawn through the system by a constant volume system (CVS) which had a flowrate of about 650 scfm. Methanol was sampled using the procedures set forth in reference 4 (the reference method for sampling and analysis of

methanol), and in accordance with procedures specified for sampling regulated FTP gaseous emissions(5). In the former case, the dilute exhaust samples were bubbled through water using impingers which were later analyzed for methanol on the GC; in the latter case the samples were collected in bags which were analyzed on the heated FID using the FBM (see Figure 1).

Evaporative emissions were sampled in a Sealed Housing for Evaporative Determination (SHED). At the conclusion of each diurnal test, samples were taken from the SHED in a 60L Tedlar bag for analyses of methanol using the GC and FBM.

The FBM procedure consisted of first using a heated FID to analyze a portion of the CVS or evaporative sample which had been collected in a bag. Next, the remaining sample in the bag was bubbled through water in two series impingers into a second bag which was re-analyzed using the same heated FID. The difference in reading between the two bags was taken as a measure of the methanol fraction absorbed in the water. Because the heated FID had been calibrated using propane, its methanol C response factor was about 0.75 ± .02. Therefore, a correction factor equal to the reciprocal of 0.75, or 1.33, was applied to the difference measurement to arrive at the concentration of methanol in the sample.

After adequate samples had been taken for methanol analysis, remaining sample portions of both the unbubbled and bubbled bags were retained as samples for separate GC analyses to obtain an accounting of the detailed hydrocarbons before and after the bubbling in water. These analyses were performed using the chromatographic procedures of Black et al. (6).

SECTION 4
RESULTS AND DISCUSSION

The FBM and the reference method were used to simultaneously collect and analyze data during FTPs with a Methanol Escort. Summaries of that data are contained in tables 2,3 and 4. The term "FID Total Organic" used in the tables refers to the FID measurement of the CVS bag sample taken before it was bubbled in water. The FID measurement of the bubbled sample is termed "HC (FBM)" and the decrease in concentration due to bubbling is termed "CH_3OH(FBM)". This decrease, adjusted to compensate for the FID's low response to methanol, represents the FBM estimate of the methanol concentration in the sample. The methanol measured using the GC in accordance with the reference method is termed "CH_3OH(GC)".

Table 2 contains data when the Escort was being fueled with M85. Comparisons between the methanol measurements with the FBM and the GC are rather poor in this table. For the CT, HS, and WT test phases of the FTP, the average differences between the CH_3OH (FBM) values and the CH_3OH (GC) values are 46%, 112%, and 55%. Similar data obtained from the same Methanol Escort operating on M100 (pure methanol) fuel are shown in Table 3. The average differences for this case are 11%, 79%, and 24%.

Evaporative emissions results obtained using M85 and M100 fuels are shown in Table 4. Evaporative tests using M85 fuel, performed with the charcoal canister disconnected, resulted in substantially higher emission rates than when the canister was connected during the M100 tests. Comparisons between the two methanol measurement methods for evaporative emission tests (average difference <25%) were somewhat improved over those for the exhaust emission tests, however, methanol determinations with the FBM were still consistently higher.

FBM methanol determinations error on the high side when final FID readings (HC (FBM)) are lower than expected. For example, absorption of some sample hydrocarbons in the water solution used to absorb methanol would result in a lower final FID reading. Because partial absorption of hydrocarbons was suspected, an attempt was made to identify and quantify the absorbed HC species. This was accomplished through detailed HC analyses of bubbled and unbubbled exhaust samples. Integrated HC results from three of these analyses (shown in Table 5) indicate that between 2 and 11 percent of the hydrocarbons were being absorbed in samples taken during the CT Test Phase of the FTP. Results from the other two test phases are less dramatic with little or no measureable absorption occurring. This finding is not unexpected since exhaust gas olefins and aromatics, which are normally more soluble in water than the paraffinic components, comprise a greater fraction of the CT Test Phase hydrocarbons.

Many hydrocarbons which are virtually insoluble in water are very soluble in alcohol. Because alcohol (methanol) is being collected in the water solution during bubbling with the FBM, the possibility exists that some hydrocarbons are being absorbed in this alcohol. Evidence suggesting this occurrence is the noticeable decrease in concentration after bubbling of cis-2-butene, 1-pentene, 2-methyl-2-butene, and o-xylene. All of these HC compounds are listed as being very soluble or miscible in alcohol but insoluble in water (7). Beyond this observation, the extent of HC absorption

in methanol with the FBM was not examined and thus remains a study for future consideration.

When the FBM methanol measurements are corrected to account for the absorption of hydrocarbons in the water solution, the results are still significantly higher than the GC values (see Table 5). This persistent discrepency led to a preliminary examination of another factor thought possibly to be impacting FID response to hydrocarbons. This was the higher water vapor in bubbled samples than in unbubbled samples. Sample humidity before bubbling, which is estimated below 50 percent, increases to saturation levels after bubbling. To examine whether or not this increase in humidity has any effect on FID response to hydrocarbons, a hydrocarbon sample collected from the Plymouth Caravelle was saturated with water vapor and analyzed on the FID (17ppm). Then the sample was dried (PermaPure Drier) and reanalyzed to determine if sample humidity had had any effect on FID response. None was observed. In another test, water was injected into a bag containing 84 ppm HC. Identical FID measurements before and after the injection again demonstrated that sample humidity levels had had no significant effect on FID response to normal exhaust hydrocarbons. Future tests are recommended to examine thoroughly the humidity effect on FID response to organic emissions samples from a methanol-fueled automobile.

Unfortunately, time restraints have ended the quest to determine the mechanisms responsible for FBM methanol measurement disparities. It is interesting to note, however, that when the FBM "error" percents presented in Table 1 are arranged in order of magnitude, the exhaust measurement errors are inversely related to the methanol content of the sample (see Table 6). Obviously, FBM accuracy in the study benefitted substantially with increase in methanol concentration of the exhaust sample.

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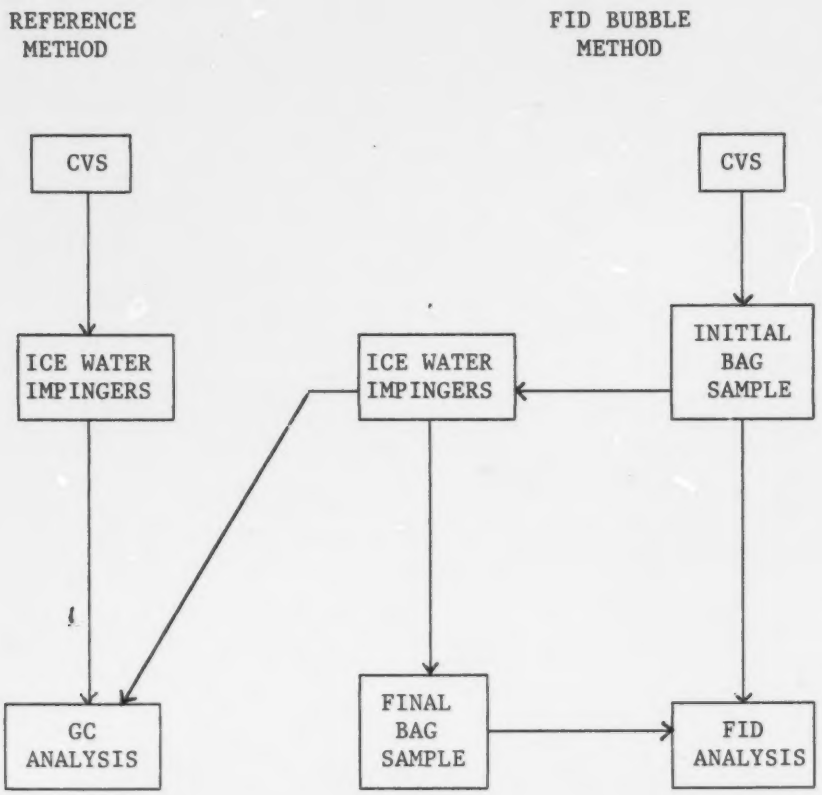

Figure 1. Methanol sampling and analysis flow schematic

TABLE 1. DIFFERENCES (IN PERCENT) OF METHANOL MEASUREMENTS, FBM VERSUS GC

TEST PHASE/FUEL:	M85	M100
Cold Transient	+46%	+11%
Hot Stabilized	+112%	+79%
Warm Transient	+55%	+24%
Diurnal	+25%	+20%

TABLE 2. FTP EXHAUST DATA, M85 FUEL

Run #	FID TOTAL ORGANIC (ppm)	HC (FBM) (ppm)	CH_3OH (FBM) (ppm)	CH_3OH(GC) (ppm)
		CT TEST PHASE		
30242	82	39	57.2	38.7
30243	82	38	58.5	41.9
30244	91	44	62.5	41.0
AVG.	85	40	59.4	40.5
		HS TEST PHASE		
30242	16	13	4.0	1.8
30243	16	13	4.0	1.8
30244	13	11	2.7	1.4
AVG.	15	12	3.6	1.7
		WT TEST PHASE		
30242	56	30	34.6	23.5
30243	56	29	35.9	22.5
30244	50	28	29.3	18.6
AVG.	54	29	33.3	21.5

TABLE 3. FTP EXHAUST DATA, M100 FUEL

Run #	FID TOTAL ORGANIC (ppm)	HC (FBM) (ppm)	CH_3OH (FBM) (ppm)	CH_3OH(GC) (ppm)
	CT TEST PHASE			
30245	173	12	214.1	200.0
30246	130	10	160.0	135.1
30248	89	8	107.7	125.7
30249	101	8	123.7	130.7
AVG.	123.2	9.5	151.4	147.9
	HS TEST PHASE			
30245	11	7	5.3	3.0
30246	10	5	6.6	3.0
30248	10	5	6.6	3.2
30249	6	4	2.7	2.4
AVG.	9.2	5.2	5.3	2.9
	WT TEST PHASE			
30245	23	7	21.3	16.0
30246	63	7	74.6	55.0
30248	45	6	51.9	44.4
30249	52	6	61.2	55.1
AVG.	45.7	6.5	52.2	42.6

TABLE 4. DIURNAL EVAPORATIVE DATA

RUN#	FUEL	FID TOTAL ORGANIC (ppm)	HC (FBM) (ppm)	CH_3OH(FBM) (ppm)	CH_3OH(GC) (ppm)	COMMENT
30240	M85	252	232	26.6	21.5	w/o canister
30234	M85	234	210	31.9	22.8	w/o canister
30237	M85	237	213	31.9	28.7	w/o canister
30250	M100	14.0	4.0	13.3	11.4	w/ canister
30251	M100	12.8	3.4	12.5	10.1	w/ canister

TABLE 5. FTP Exhaust Data, M85 Fuel

Run #	Integrated THC (GC) Unbubbled (ppm)	Integrated THC (GC) Bubbled (ppm)	HC's Absorbed In Water (ppm)	CH_3OH(FBM) Corrected for HC's Absorbed (ppm)	CH_3OH (GC) (ppm)
			CT TEST PHASE		
30242	39.3	36.8	2.5	53	39
30243	38.6	34.2	4.4	52	42
30244	40.1	39.4	0.7	61	41
			HS TEST PHASE		
30242	11.6	11.3	0.3	3.6	1.8
30243	10.3	11.1	-	4.0	1.8
30244	9.9	9.5	0.4	2.2	1.4
			WT TEST PHASE		
30242	27.8	27.2	0.6	34	23
30243	26.6	27.1	-	36	22
30244	24.3	24.7	-	39	19

TABLE 6. METHOD COMPARISON VS. METHANOL FRACTION AND CONCENTRATION IN EXHAUST SAMPLES

Methanol Fraction	Methanol Conc. (ppm)	% Diff. (FBM Error)
.11	2	+112%
.29	3	+79%
.36	21	+55%
.43	40	+46%
.76	43	+24%
.92	148	+11%